Photochemical Deazetation of 2,3-Diazabicyclo[2.2.2]oct-2-ene: Pseudorotation of the Cyclohexanediyl Biradical

Andrew J. F. Edmunds and Christopher J. Samuel *
Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

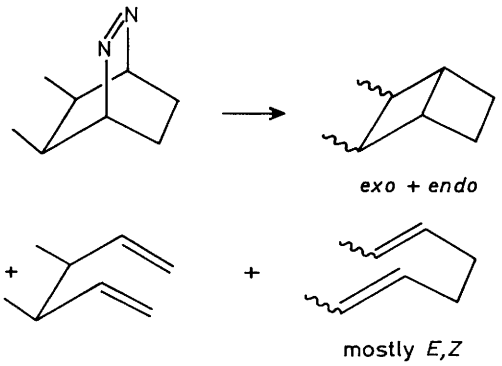
Direct irradiation of *cis-anti*-[5,6-$^2H_2$]-2,3-diazabicyclo[2.2.2]oct-2-ene leads to bicyclohexane in which the deuterium is predominantly *exo*, *i.e.* with inversion of configuration, to hexadiene in which most, but not all, of the vinylic deuterium is present in the *E,Z*-isomer, and to cyclohexene lacking vinylic deuterium. Qualitatively similar results were obtained for the sensitised irradiation. The results are discussed in terms of a scheme in which cleavage of one C–N bond is followed by conformational changes in a diazenyl biradical, and then in a cyclohexanediyl biradical.

2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) and a number of compounds containing that substructure have been termed 'reluctant azo alkanes'[1] because of the relatively low quantum yield for loss of nitrogen on direct or sensitised irradiation, and also the relatively high temperature needed to expel nitrogen thermally. Many aspects of their chemistry have been investigated,[2] including product studies, which usually show hexadienes and bicyclohexanes (BCH's), *e.g.* Scheme 1, in proportions which depend on the substitution pattern.[3] The only stereochemical investigation of a simply substituted member of the series is that of Roth and Martin,[4] who studied the thermolysis of the dimethyl-DBO's (Scheme 1), but there are some difficulties in interpretation of these results which are discussed below.

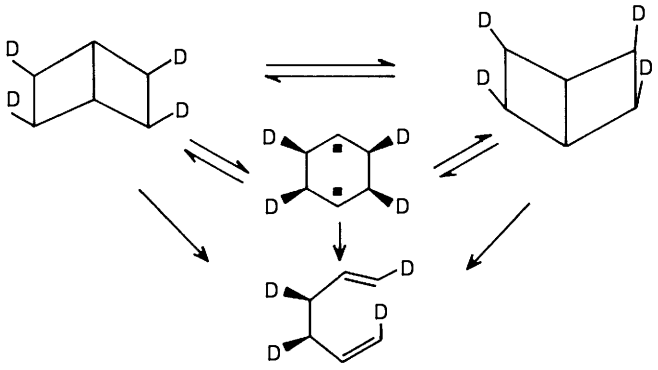
Clearly related to this are the studies of the stereochemistry of the pyrolysis of bicyclohexanes. Paquette and Schwartz[5] reported cleavage to form hexadienes with inversion of stereochemistry at one of the double bonds, while Goldstein and Benzon[6] were the first to report both the stereochemistry of cleavage and the envelope inversion of bicyclohexane itself (Scheme 2). They were cautious in not attempting to distinguish between concerted and biradical mechanisms, and in not attempting to discuss the conformations of any possible biradical intermediate. Others, however, have postulated a chair[5] or a twist[7] conformer of cyclohexanediyl.

The relationship of the Cope rearrangement to these studies is more questionable. Gajewski[8] has argued that the Cope transition state is lower in energy than the transition state(s) for the inversion and cleavage of BCH, and thus the reactions cannot proceed by related pathways. Doering[9] postulated a cyclohexanediyl intermediate in the Cope rearrangement, and Dewar's MO calculations appeared to confirm this.[10] However, on the basis of secondary deuterium kinetic isotope effects, Gajewski and Conrad[11] argued that the reaction was concerted, and the transition state structure changes with the substitution.

It seemed that a study of the deazetation of a stereochemically labelled DBO would be a useful contribution to this area, provided that it was sterically unbiased, suggesting the use of deuterium as a stereochemical label, and avoided the ambiguities inherent in the thermal reaction, discussed below, suggesting a need to concentrate on the photochemical route. We have recently given a preliminary report[12] of the stereochemistry of formation of BCH, and give here full details of that work, together with a stereochemical analysis of the other products of the reaction.



Scheme 1.

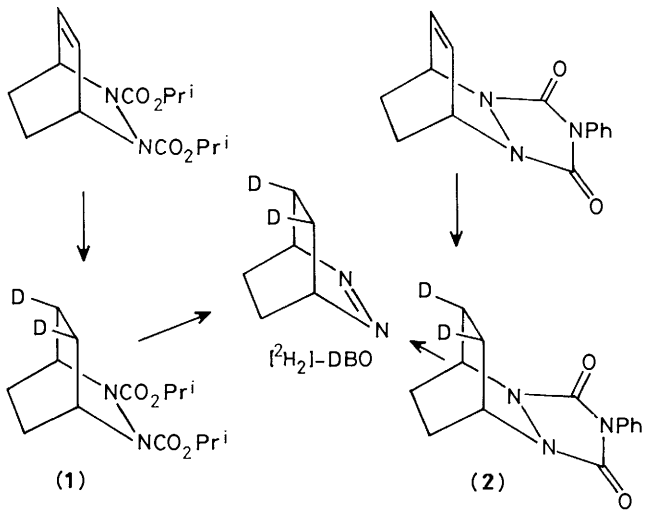


Scheme 2.

Results

Synthesis and Stereochemical Assignment of Reactant.—The stereospecifically deuteriated azo compound was approached from two precursors, as shown in Scheme 3. The biscarbamate (**1**) showed a consistently higher degree of stereospecificity than the urazole (**2**), but gave problems in the n.m.r. analysis because most of the signals were doubled, presumably because of restricted rotation about the amide bonds, so both precursors were important in the analysis.

The initial stereochemical assignments were on the basis of lanthanide induced shift (l.i.s.) studies of DBO and the urazole (**2**), assuming that protons *syn* to the heteroatoms would be more strongly shifted than those *anti*. This led to the assignments given in Table 1. Deuteriated samples were used to



Scheme 3.

Table 1. ^1H and ^2H N.m.r. data (δ) for deuteriated compounds

Deuteriated compound	^1H N.m.r. shifts and assignments: Deuteriated position	Geminal partner	^2H N.m.r. signals: Shifts	Ratio
(**1d**)	1.34 and 1.78 (*anti*)	1.78 and 2.09 (*syn*)	1.39 and 1.78 only	>99 : 1
DBO from (**1d**)	1.55 (*anti*)	1.27 (*syn*)	1.52 only	>99:1
(**2**)	1.84 (*anti*)	2.10 (*syn*)	1.85, 2.09	68:32
DBO from (**2d**)	1.55 (*anti*)	1.27 (*syn*)	1.52, 1.23	68:32

Table 2. ^2H N.m.r. analysis of cyclohexene from DBO

% Of total deuterium at the *anti* position of $[^2H_2]$-DBO	% Of total deuterium at the vinyl position of cyclohexene
100	0
68	10
40	17

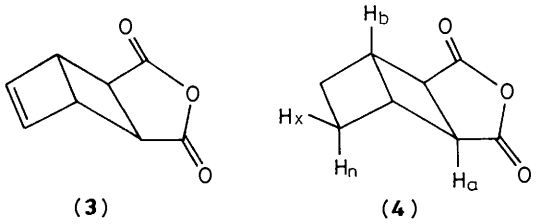
correlate assignments for DBO, (**1**) and (**2**), and to show that these were mutually consistent. These results are also in Table 1. Thus, a sample of (**2**) which showed two signals in the ^2H n.m.r. in the ratio of 68:32 with the major signal at δ 1.85 (assigned as *anti* by l.i.s. on the ^1H n.m.r.) gave DBO which also showed two signals in the ^2H n.m.r. in the ratio of 68:32 with the major signal at δ 1.52 (also assigned as *anti* by l.i.s. on the ^1H n.m.r.). In a similar way, (**1**) and DBO were also correlated.

On this basis, we concluded that addition of deuterium had taken place predominantly to the face of the double bond *anti* to the heteroatoms. The greater stereospecificity of formation of the carbamate (**1**) was thus attributable to the steric bulk of the isopropyl groups. This did, however, contrast with our work on deazetation of 7,8-diazabicyclo[4.2.2]dec-7-ene where deuterium added to the urazole precursor to the face of the double bond *syn* to the heteroatoms.[13] Furthermore, the results described below were sufficiently surprising for us to wish to confirm our assignments.

Accordingly, we carried out a $^{15}N\{^1H\}$ nuclear Overhauser effect (n.O.e.) study of urazole (**2**). The ^{15}N n.m.r. of (**2**) showed two signals in the ratio of 2:1. The smaller, at δ −230 attributed to the phenylated nitrogen, was used as a standard, and the larger at δ −244 showed a −40% n.O.e. on irradiation in the ^1H region at δ 2.10, previously assigned as *syn*, but none on irradiation at δ 1.84, assigned as *anti*. We took this as sufficient confirmation of our assignments.

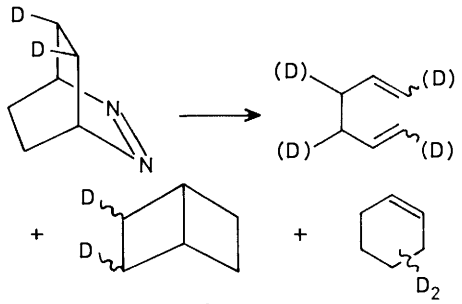
Stereochemical Assignments of the Products.—Assignment of the terminal vinyl signals in the ^1H n.m.r. of hexadiene is implicit in the report of Goldstein and Benzon,[6] and is unambiguous because the lower field signal shows the larger coupling constant and is thus due to the *cis*-proton.

We originally accepted Goldstein and Benzon's assignment of the ^1H n.m.r. spectrum of BCH which was based on the expectation of *exo* addition of deuterium to the unsaturated anhydride (**3**).[14] While this seemed highly probable, we again



felt the need to confirm this assignment, and prepared the saturated anhydride (**4**) by their route and subjected it to l.i.s. and $^1H\{^1H\}$ n.O.e. studies, which are detailed in the Experimental section, and which were fully consistent with the original assignment.

^2H N.m.r. Analysis of Products.—Direct and sensitised photolysis of $[^2H_2]$-DBO (Scheme 4) gave hexadiene which showed signals in the ^2H n.m.r. spectrum attributable to the allylic and terminal vinylic positions in the ratio of 1.00 ± 0.02. The ratio of the signals due to the *cis* and *trans*



Scheme 4.

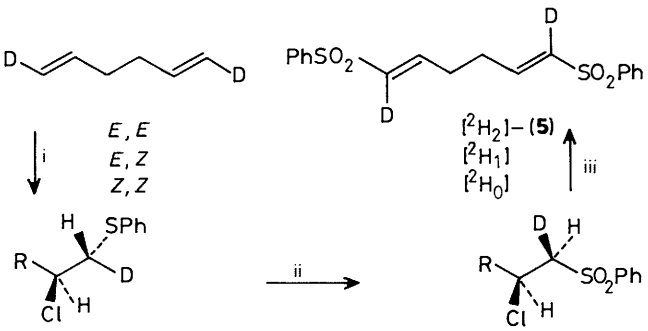
terminal positions was 1.00 ± 0.03. The bicyclohexane showed signals attributable to the *exo* and *endo* positions in the ratio of 83:17 from the direct and 58:42 from the sensitised photolysis. Cyclohexene was formed only on direct irradiation and showed a deuterium distribution which depended on the stereochemical purity of the starting DBO as shown in Table 2.

Complete Stereochemical Analysis of the Hexadiene.—On the basis of the ^2H n.m.r. results, we can only state that the ratio of *E* to *Z* deuterium in the hexadiene was approximately unity, but, as we have noted,[15] ^2H n.m.r. cannot give the distribution among the *E,E*, *E,Z*, and *Z,Z* isotopomers. However, we have recently developed a combination of a four-step chemical derivatisation and mass spectrometry which is able to do so. We report here the results of applying this new method to the hexadiene formed on sensitised and direct irradiation of $[^2H_2]$-DBO (Table 3).

The essence of the method[15] is that a stereospecific

Table 3. Stereochemical analysis of products

Product	Observation	*hν*(direct)	*hν*(sens)	Pyrolysis(BCH)
BCH (by ^2H n.m.r.)	% *exo*-[$^2H_2$]	83	58	
	% *endo*-[$^2H_2$]	17	42	
Hexadiene (by chemistry + m.s.)	% *E,E*-[$^2H_2$]	13	15	15
	% *E,Z*-[$^2H_2$]	83	80	81
	% *Z,Z*-[$^2H_2$]	4	5	4



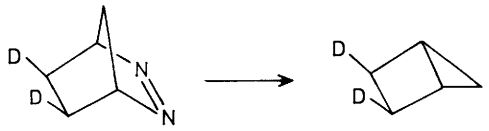
Scheme 5. *Reagents:* i, PhSCl, CH_2Cl_2; heat, DMSO; ii, MCPBA, CH_2Cl_2; iii, NaOAc, DMSO

substitution reaction as shown in Scheme 5 converts stereochemical information into deuterium content. The analysis is slightly more complex in this case than in the case of [1,8-$^2H_2$]octa-1,7-diene, since 50% of the deuterium in the hexadiene is in the allylic position, introducing the need for an extra correction step. A more serious concern was that some of this deuterium might be washed out by base-catalysed exchange in the elimination reaction. To check for this, a sample of the bis(chlorosulphone) was divided into two, one portion was subjected to the normal elimination conditions, with a reaction time of 1 h, while the other was subjected to the same conditions but for a reaction time of 24 h. The percentages of [$^2H_0$], [$^2H_1$], and [$^2H_2$] material in the two samples of disulphone (**5**) were identical within 0.5%.

For comparison purposes we also applied the method to the hexadiene formed by pyrolysis of [$^2H_2$]-BCH (76:24 *exo*:*endo*) and this result is also given in Table 3.

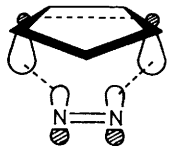
Discussion

Bicyclohexane Formation.—Most significantly, *anti*-[$^2H_2$]-DBO gives predominantly *exo*-[$^2H_2$]-BCH. This corresponds to inversion of configuration. While a similar result was reported 20 years ago[16] for the next lower homologue, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and more recently for 2,3-diazabicyclo[2.1.1]hex-2-ene,[17] it has only been observed for compounds containing the DBO substructure in cases in which retention would give the thermodynamically disfavoured isomer.[18,19] The present study is the first sterically unbiased case of a DBO to show this behaviour.

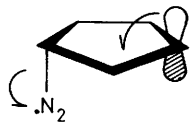


Scheme 6.

A number of suggestions have been made to explain the DBH result,[16,20–23] but most of them require that at some stage the five carbons of the ring become planar. This is implied by both the recoil mechanism,[21] and the concerted $\sigma^2_a + \sigma^2_a$ mechanism (**6**), in which the nitrogen leaves from one side and the back lobes of the orbitals on carbon overlap simultaneously to form the new bond in the bicyclopentane.[16] In the present case, mechanisms analogous to these would require almost complete planarisation of the six carbons of the ring and would be energetically very costly. More applicable is the mechanism originally postulated by Roth and Martin,[20] and more recently extended by Adam,[23] in which one C–N bond cleaves to afford a diazenyl biradical which undergoes C–C bond formation by backside attack on the other C–N bond (**7**).



(**6**)



(**7**)

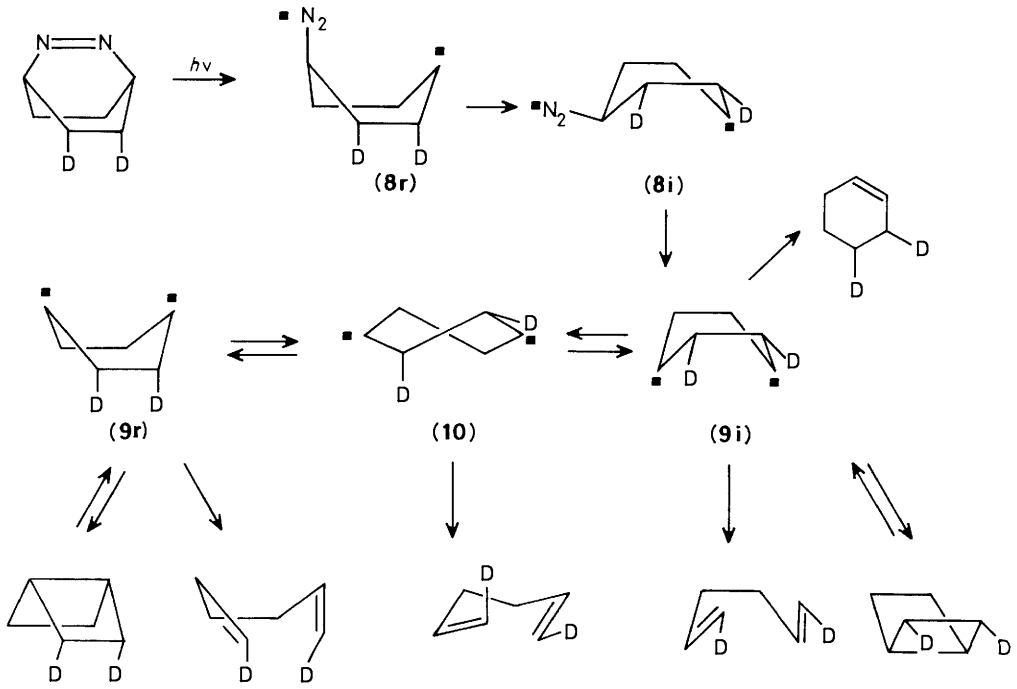
We thus suggest that our results are best accounted for by a mechanism in which one C–N bond cleaves to give a diazenyl biradical in a boat conformation (**8r**)[24] which would be expected to relax to a twist conformer, but is shown as a boat in Scheme 6 for clarity, and referred to as such in the text. In this the diazenyl group is in the flagpole position, but conformational interconversion will move it to the bowsprit position, giving a more stable conformation (**8i**). Loss of nitrogen and ring closure (or possibly S_Hi) will lead to the preferred inverted BCH. The retained BCH may arise in a similar way from (**8r**) or by back equilibration of the cyclohexanediyls (**9**) and ring closure.

One Bond or Two Bond Cleavage.—The question of one bond or two bond cleavage in the deazetation of azo compounds has long been a contentious issue.[2] A number of theoretical papers[25,26] have concluded that the two bonds cleave sequentially, though the highest level calculations[26] have been performed on the parent diazene where the second bond is NH rather than NC and is likely to be stronger, favouring the stepwise process.

For cyclic and polycyclic azo compounds, the experimental evidence for one bond cleavage seems to be strongest for those in which the azo group is part of a five-membered ring, and is of several types. Firstly, several cases have been reported in which allylic inversion in β,γ-unsaturated azo compounds occurs.[27] It is suggested that the initially formed diazenyl radical rebonds to the other end of the allyl radical. Secondly, in a number of cases,[28] pyrazolines undergo retro-3 + 2 cycloaddition to give a diazo compound, in competition with loss of nitrogen. The most reasonable mechanism is a stepwise pathway, in which a diazenyl biradical partitions between N–C and C–C cleavage. Thirdly, Dougherty[29] has used chemical activation and RRKM calculations to assess the energy partitioning between nitrogen and the hydrocarbon fragment, and concluded that there is a diazenyl biradical intermediate. Fourthly, some unusual stereochemical results, such as that for the deazetation of DBH,[16] for which S_Hi with inversion has been postulated,[20] are best interpreted in terms of diazenyl biradicals.

When the azo group is part of a six-membered ring, there is less evidence for one bond cleavage. Engel[30] has applied the Rampsberger criterion to the thermal reaction, and finds cumulative rate enhancements for non-conjugating substituents, implying that both bonds are equally broken in the rate determining step and thus either two bond cleavage occurs, or there is reversible cleavage of one. He has also shown a very approximate linear free energy relationship between the thermal and photochemical rates, suggesting closely related mechanisms.[3]

The only complete set of rate data, in the literature, for the

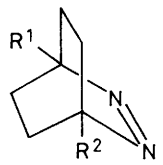


Scheme 6.

Table 4. Data for cyclopropyl substituted DBO (**11**)

R^1, R^2	k_{rel} (230.5 °C)	φ_{-N_2}	τ_f/ns	$k_{-N_2} \times 10^{-4}$ s^{-1}
H, H	1.00	0.018	436	4.13
H, c-C_3H_5	4.27	0.16	402	39.8
(c-C_3H_5)$_2$	18.4	0.16	632	25.3

photochemical reaction, which permit application of the Rampsberger criterion, is for the cyclopropyl substituted compounds (**11**)[31] (Table 4, which also includes comparative



(**11**)

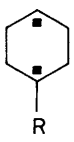
data for the thermal reaction[30]). For the photochemical reaction, there is a rate enhancement for the first substitution, but not for the second, suggesting that only one bond is cleaved in the rate determining step. These considerations are consistent with two bond cleavage in the thermal and one bond cleavage in the photochemical processes.

We have needed to postulate one bond cleavage in the present photochemical deazetation to account for the unusual stereochemistry observed, and it is tempting to compare our results with Roth's study[4] of an analogous thermal reaction (Scheme 1), in order to test the suggestion that the thermal and photochemical deazetations proceed by different mechanisms. Unfortunately, it is not clear, in the thermolysis, whether the dienes are formed directly from the azo compounds or from the bicyclohexanes, and whether the latter interconvert. Using literature data for the unsubstituted compounds, half-lives for various processes can be calculated at 220 °C: loss of nitrogen from DBO:[32] 2.5 × 10^5 s, cleavage of BCH:[6] 260 s, inversion of BCH:[6] 115 s, Cope rearrangement of hexadiene:[9] 4.5 × 10^5 s. Secondary reactions are thus expected to be a major problem.

Hexadiene Formation.—Firstly, the major isotopomer of the hexadiene is *E,Z* in all cases. This cannot arise from a boat biradical (**9i**) or (**9r**) or a nearby twist, which could only lead to *E,E* or *Z,Z* diene, but requires relaxation to the 90° twist conformation (**10**), or possibly to the chair. Secondly, significant amounts of the *E,E* isomer are formed, indicating that at least some cleavage occurs from the initially formed boat radical (**9i**). Thirdly, while some *Z,Z* isomer is formed, the *E,E* is more abundant, *i.e.* double inversion is preferred, and, while the error in the numbers is probably quite large, this was our consistent observation, in every run. This preference for inversion is the same as in the formation of BCH and provides further support for a mechanism in which the first-formed cyclohexanediyl is inverted.

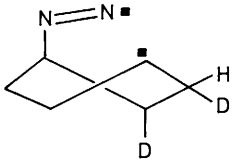
For comparison, we reinvestigated the stereochemistry of the thermal conversion of BCH to hexadiene and find it to be very similar to the photolysis of DBO. We concur with the original report[6] in finding predominant formation of the *E,Z* isomer, but also find small amounts of the *E,E* and *Z,Z*, which might not have been detected by their analysis, which depended ultimately on the i.r. spectra of *meso*- and (±)-[$^2H_2$]succinic acids from oxidation of hexadiene. In this case, the observation that *E,E* > *Z,Z* implies retention of configuration, consistent with Scheme 6, in which (**9i**) and (**9r**) are formed directly by bond cleavage without the preliminary inversion postulated to occur *via* the diazenyl biradical.

Cyclohexene Formation.—Previous studies of DBO[3,33,34] have not reported the formation of cyclohexene, though it was observed as a product from the analogous 1,1-diazene.[35] It is only formed in low yield and, on all our g.c. columns, it co-chromatographed with BCH, which may account for it having been overlooked previously. It is noteworthy that it is produced only in the direct irradiation experiments, and not sensitised irradiation or pyrolysis of either DBO or BCH.



(13)

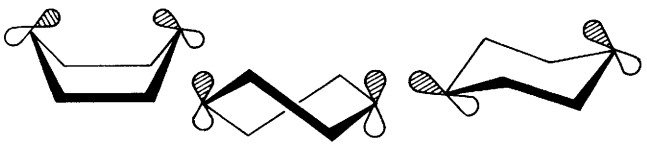
a; R = H
b; R = Ph
c; R = c-C_3H_5



(12)

The labelling pattern reported in Table 2 permits determination of the stereochemistry of the hydrogen which migrates to form the cyclohexene, which turns out to be exclusively *anti* to the heteroatoms. A primary kinetic isotope for the hydrogen migration of $k_H/k_D = 2.7$ gives confidence in the analysis, but the high stereospecificity is surprising. It would have been possible to account for exclusive *syn* migration if a hydrogen atom were abstracted by the terminal nitrogen of the diazenyl biradical as in (**12**) and then nitrogen were lost without further hydrogen shifts. However, selective abstraction of an *anti*-hydrogen (or deuterium) by the diazenyl biradical would appear to be impossible, and a mechanism involving a hydrogen shift in the cyclohexanediyl must be involved. Furthermore, while not wishing to rely too heavily on a minor product to establish the mechanism, since this reaction is so stereospecific, the cyclohexene, at least, must come from a diyl that is formed stereospecifically, *i.e.* (**9i**) must be formed stereospecifically.

Conformational Analysis of the Diyl Triplet Lifetimes.—Adam[36] has recently reported the lifetime of triplet phenylcyclohexanediyl (**13b**) (250 ns), and noted that this is much longer than that of the parent (**13a**) (0.1 ns).[37] In the 1987 paper,[36] they suggest that, after loss of nitrogen, the biradicals are born in a boat conformation (**14**) in which intersystem crossing (i.s.c.) is predicted to be fast, and that for (**13a**), i.s.c. and product formation occur rapidly at or near this initial geometry. On the other hand, for (**13b**), phenyl stabilisation provides sufficient time for relaxation to a twist boat (**15**) for which i.s.c. is predicted to be slower. Cleavage from (**14**) would imply that deazetation of [$^2H_2$]-DBO would give hexadiene which did not contain the *E,Z*-[$^2H_2$]-isomer, since this can only arise from a relaxed geometry such as the twist (**15**) or chair (**16**) (Scheme 6).



(14) (15) (16)

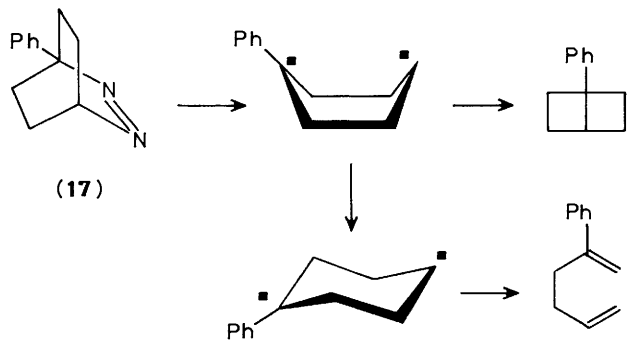
The formation of the *E,Z*-isomer, reported here, is much more consistent with the discussion of conformational changes in their 1984 paper,[37] in which they used cyclohexane as a model in order to estimate rates of conformational interconversion. They estimate that triplet (**13a**) should undergo substantial pseudorotation on the boat-twist circuit even during its short lifetime, but should not have time to convert into the chair. Our results, which show that BCH is formed with some stereochemical memory, imply that equilibration on the twist-boat pseudorotation circuit is not complete.

An alternative explanation in which i.s.c. occurs at the initial geometry followed by product formation on the singlet surface could account for the stereochemistry of the diene but not for that of the bicyclohexane which differs substantially between the direct and sensitised photolyses.

Following Adam,[37] we assume that the barriers to conformational interconversion are the same for the biradical as for cyclohexane itself. Thus the rate at which the biradical would visit the boat-twist pseudorotation circuit is 4×10^{11} s^{-1} (E_a = 8 kJ mol^{-1})[38] and would convert to the chair is 1.4×10^9 s^{-1} (E_a = 22).[39] Thus, even with a lifetime of 0.1 ns, triplet (**13a**) should be able to visit most of the boat-twist circuit, though probably not the chair, whereas triplet (**13b**) even has time to reach the chair. We thus suggest that (**13a**) remains on the boat-twist pseudorotation circuit where it passes through regions of high i.s.c. efficiency, whereas (**13b**) can reach the chair. Once it does so, the rigidly parallel orbitals imply slow i.s.c. and a long lifetime since there is unlikely to be any back reaction ($k = 1.3 \times 10^5$ s^{-1}, E_a = 45).[40]

Engel[3] gave a similar explanation in terms of boat and chair biradicals (**13b**), for his observation that direct irradiation of (**17**) gave only cleavage and not the coupling product (Scheme 7).

The singlet cyclohexanediyl (**13a**), which is expected to have an even shorter lifetime [$\times$ 11 in the case of Engel's cyclopropyl compound (**13c**)[31]], still undergoes substantial conformational relaxation, though clearly less than the triplet, consistent with the operation of a spin correlation effect.



(17)

Scheme 7.

Conclusions.—The predominant inversion of stereochemistry in the bicyclohexane from photochemical deazetation of diazabicyclo-octene seems to require the intermediacy of the diazenyl biradical, which has a lifetime long enough to undergo some conformational change before loss of nitrogen. The stereochemistry of the cleavage product requires that a cyclohexanediyl biradical can also undergo conformational change.

Experimental

^1H N.m.r. spectra were recorded on a Perkin-Elmer R34 at 220 MHz. Chemical shifts are reported in p.p.m. downfield from internal tetramethylsilane. ^2H N.m.r. spectra were recorded on a Bruker WH400 at 61.4 MHz. Chemical shifts are reported relative to internal $CDCl_3$ = 7.24 p.p.m. N.O.e. experiments, both $^{15}N\{^1H\}$ and $^1H\{^1H\}$, were also carried out on this instrument. I.r. spectra were recorded on a Perkin-Elmer 680B machine and u.v. spectra on a Perkin-Elmer 552. Mass spectra were recorded on a Kratos MS80 instrument. Analytical gas chromatography was performed using packed columns and nitrogen as carrier on a Pye Unicam 204, or using capillary columns and helium as carrier on a Carlo Erba 2450TP, fitted with a Grob type split/splitless injector. Preparative g.c. was performed using the latter instrument fitted with 4 or 10 mm diam. columns. M.p.s were uncorrected. Elemental analyses were carried out by Butterworth Laboratories, Teddington, Middlesex. Pentane refers to n-pentane purified by extraction with concentrated sulphuric acid, washing with water, passage through a column of alumina, and distillation through a 500 mm Vigreux column. Alumina refers to alumina, activity I for chromatography.

Table 5. Deuterium content and stereochemistry

Precursor	Catalyst	Solvent	$[^2H_0]:[^2H_1]:[^2H_2]$ by m.s.	*anti*:*syn* by ^2H n.m.r.
(**2**)	PtO_2	EtOAc	18:30:52	86:14
	PtO_2	EtOH	>90%[$^2H_0$]	74:26
	Pd/C	Benzene	1:11:88	68:32
(**1**)	PtO_2	EtOAc	32:42:26	97: 3
	Wilkinson's	Toluene	0: 1:99	80:20
	Pd/C	EtOAc	1: 9:90	>99: 1
	Pd/C	Benzene	0: 7:93	>99: 1
	N_2D_2	EtOD	3:27:70	40:60

Table 6. N.O.e. enhancements observed for (**4**)

Irradiated signal	% Signal enhancement at δ			
	3.54	3.13	2.74	2.25
δ 3.54		3.1	<1	2.6
3.13	1.3		1.9	<1
2.74	<1	4.7		10.9
2.25	1.5	<1	5.8	

4-*Phenyl*-2,4,6-*triazatricyclo*[5.2.2.0^{2,6}]*undec*-8-*ene*-3,5-*dione*.—The procedure of Gillis and Haggarty[41] was followed except that the 4-phenyl-1,2,4-triazolidine-3,5-dione was oxidised using t-butyl hypochlorite rather than lead(IV) acetate.[15] 4-Phenyl-1,2,4-triazolidine-3,5-dione (4.40 g, 25 mmol) gave 4-phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (5.51 g, 90%), m.p. 170—172 °C (lit.,[41] 170—171 °C).

4-*Phenyl*-2,4,6-*triazatricyclo*[5.2.2.0^{2,6}]*undecane*-3,5-*dione*.—4-Phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (2.55 g, 10 mmol), 10% palladium on carbon (0.1 g), and benzene (250 cm^3) were stirred under an atmosphere of hydrogen in a conventional hydrogenator, until uptake of hydrogen ceased. Filtration through Celite and concentration under reduced pressure gave 4-phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undecane-3,5-dione (2.55 g, 100%), m.p. 211—212 °C (from EtOH) (lit.,[41] m.p. 211—212 °C); $\nu_{max.}$(mull) 1 760 and 1 700 cm^{-1}; $\delta_H(CCl_4)$ 1.80—2.20 (8 H, AA′BB′ part of AA′BB′XX′), 4.43 (2 H, br s), and 7.31—7.58 (5 H, m). The highfield region clearly fell into the AA′ and BB′ parts but could not be analysed completely: *m*/*z* (e.i.) 257 (M^+, 35%), 228 (26), and 119 (100).

[8,9-$^2H_2$]-4-*Phenyl*-2,4,6-*triazatricyclo*[5.2.2.0^{2,6}]*undecane*-3,5-*dione*.—Replacement of hydrogen by deuterium in the procedure above gave a product showing the appropriate differences in its ^1H n.m.r. spectrum; $\delta_D(CHCl_3)$ 1.84 (68%) and 2.10 (32%); m.s., after correction for natural abundance of heavy isotopes, showed [$^2H_0$] (1.0%), [$^2H_1$] (11.3), [$^2H_2$] (87.7).

[5,6-$^2H_2$]-2,3-*Diazabicyclo*[2.2.2]*oct*-2-*ene from* (**2d**).—Using the general procedure of Adam,[42] (**2d**) (0.76 g, 3 mmol) gave, after sublimation (80 °C, 20 mmHg), [5,6-$^2H_2$]-2,3-diazabicyclo[2.2.2]oct-2-ene (0.26 g, 81%), m.p. 141—142 °C (lit.,[43] m.p. 141.4 °C). The product showed the appropriate differences in its ^1H n.m.r. spectrum; $\delta_D(CHCl_3)$ 1.27 (32%) and 1.55 (68).

Di-isopropyl 2,3-*Diazabicyclo*[2.2.2]*oct*-5-*ene*-2,3-*dicarboxylate*.—Using the photochemical procedure of Askani,[44] cyclohexa-1,3-diene (3.5 g, 44 mmol) and di-isopropyl azodicarboxylate (7.96 g, 39 mmol) gave the crude title compound (10.5 g, 95%), pure by n.m.r., m.p. 101.5—102.5 °C (from hexane–chloroform) (Found: C, 59.5; H, 8.05; N, 9.9. $C_{14}H_{22}N_2O_4$ requires C, 59.55; H, 7.85; N, 9.92%); $\nu_{max.}$(mull) 1 740 and 1 720 cm^{-1}; $\delta_H(CCl_4)$ 1.24 (12 H, d, *J* 6 Hz), 1.37—2.10 (4 H, m), 4.89 (2 H, br s), 4.94 (2 H, septet, *J* 6 Hz), and 6.57 (2 H, br s); *m*/*z* (e.i.) 282 (M^+, 23%), 196 (M^+, 32), 154 (76), 126 (38), 81 (84), and 43 (100).

Di-isopropyl 2,3-*Diazabicyclo*[2.2.2]*octane*-2,3-*dicarboxylate*.—Di-isopropyl 2,3-diazabicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate (2.40 g, 8.52 mmol), 10% palladium on carbon (0.1 g), and benzene (250 cm^3) were stirred under an atmosphere of hydrogen until uptake of hydrogen ceased. Filtration through Celite and concentration under reduced pressure gave the title compound (2.40 g, 100%), pure by n.m.r., m.p. 83—84 °C (from hexane–chloroform) (Found: C, 59.2; H, 8.7; N, 9.8. $C_{14}H_{24}N_2O_4$ requires C, 59.13; H, 8.50; N, 9.85%); $\nu_{max.}$(mull) 1 740 and 1 720 cm^{-1}; $\delta_H(CCl_4)$ 1.28 (12 H, d, *J* 6 Hz), 1.32—2.20 (8 H, m), 4.14 (2 H, br s), and 4.89 (2 H, septet, *J* 6 Hz); *m*/*z* (e.i.) 284 (M^+, 5%), 198 (14), 136 (100), 111 (53), and 43 (24).

Di-isopropyl [5,6-$^2H_2$]-2,3-*Diazabicyclo*[2.2.2]*octane*-2,3-*dicarboxylate: Catalytic Deuterogenation*.—The above procedure was carried out, replacing hydrogen by deuterium, and using various combinations of solvent and catalyst. In every case the yield was quantitative, and the ^1H n.m.r. showed the expected differences. Analysis for deuterium stereochemistry, by ^2H n.m.r. and for deuterium content by m.s., after correction for natural abundance of heavy isotopes, are given in Table 5.

Di-isopropyl [5,6-$^2H_2$]-2,3-*Diazabicyclo*[2.2.2]*octane*-2,3-*dicarboxylate: Deuteriodi-imide*. Potassium azodicarboxylate was slurried with ethan[$^2H_1$]ol, concentrated under reduced pressure and dried over phosphoric oxide. Potassium azodicarboxylate (2.08 g, 10.6 mmol), di-isopropyl 2,3-diazabicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate (1.20 g, 4.26 mmol), and ethan[$^2H_1$]ol (5 cm^3) were stirred under nitrogen in oven-dried glassware, and [*O*-$^2H_1$]acetic acid was added by syringe pump (150 mm^3 h^{-1}) until the yellow colour was discharged. The mixture was diluted with water and extracted with dichloromethane, which was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated under reduced pressure to give a white solid. Since n.m.r. analysis showed 72% reduction, this material was recycled three times to give complete reduction. The yield was 1.04 g (85%), m.p. 84—85 °C (from hexane–chloroform). The deuterium analysis is also given in Table 5.

2,3-*Diazabicyclo*[2.2.2]*oct*-2-*ene from* (**1h**).—A solution of di-isopropyl 2,3-diazabicyclo[2.2.2]octane-2,3-dicarboxylate (0.5 g, 1.76 mmol) in chloroform (2 cm^3) was stirred under nitrogen in the dark. Iodotrimethylsilane (1.06 g, 5.3 mmol) was added and the mixture was heated 3 h under reflux. The mixture was concentrated under reduced pressure, treated with deoxygenated methanol (5 cm^3), and crushed ice (5 g). The procedure for isolation of the product *via* the copper complex followed that of Adam.[42] Sublimation gave 2,3-diazabicyclo[2.2.2]oct-2-ene (81 mg, 42%), m.p. 141—142 °C (lit.,[43] m.p. 141.4 °C).

[5,6-$^2H_2$]-2,3-*Diazabicyclo*[2.2.2]*oct*-2-*ene from* (**1d**).—The above procedure gave [5,6-$^2H_2$]-2,3-diazabicyclo[2.2.2]oct-2-ene in comparable yields.

N.O.e. Study of cis-exo-*Bicyclo*[2.2.0]*hexane*-2,3-*dicarboxylic Anhydride*.—The anhydride (**4**) shows $\delta_H(CDCl_3)$ 2.25 (2 H, m), 2.74 (2 H, m), 3.13 (2 H, m), and 3.54 (2 H, m). Even at 400 MHz, the coupling pattern was poorly resolved and unassignable but n.O.e. difference spectra were obtained as shown in Table 6. Enhancements were observed for most pairs, so those that were not are significant: 3.54/2.74 showed no n.O.e. in either direction, which is consistent with their assignment as H_α and H_χ; 3.13/2.25 showed no n.O.e. in either direction, which is consistent with their assignment as H_β and H_n.

General Procedure for Photochemical and Thermal Reactions.—[5,6-$^2H_2$]-2,3-Diazabicyclo[2.2.2]oct-2-ene in pentane was irradiated with a 500-W medium-pressure mercury lamp for the direct photolysis, the reaction being monitored by u.v. spectroscopy by the disappearance of the azo $n\pi^*$ band at 375 nm. For sensitised photolysis, 3-methoxyacetophenone was added as sensitiser, and irradiation was in a Rayonet apparatus fitted with '300 nm' lamps. Careful consideration of the u.v. spectra and lamp output showed that essentially all the light was absorbed by the sensitiser, and none by the azo compound. Thermal reactions were carried out in Carius tubes sealed under nitrogen.

The solution from these reactions was passed down a column of alumina (200 × 10 mm), which was flushed with more pentane. This removed sensitiser, residual azo compound, and any oxidation products. The eluant was concentrated through a 200 × 10 mm fractionating column packed with glass helices, to a volume of 1—2 cm^3. In spite of care, some of the hexadiene (b.p. 60 °C) was lost, so proportions of products are not available from ^2H n.m.r. The residue was analysed by g.c., or ^1H and ^2H n.m.r. spectroscopy, or, where appropriate, separated by preparative g.c. for further analysis.

(E,E)-1,6-*Bisphenylsulphonylhexa*-1,5-*diene.*—Benzenesulphenyl chloride was made from *N*-chlorosuccinimide (1.34 g, 10 mmol) and thiophenol (1.10 g, 10 mmol) in dichloromethane (10 cm^3) by the procedure of Fuchs.[4,5] Hexa-1,5-diene was added dropwise until the orange colour was discharged. The mixture was concentrated under reduced pressure, stirred with carbon tetrachloride (20 cm^3), filtered, and reconcentrated to give a pale yellow oil. At this stage, n.m.r. analysis suggested a 70:30 mixture of anti-Markovnikov and Markovnikov adducts.

The crude mixture was dissolved in dry dimethyl sulphoxide (5 cm^3) and heated 2 h at 100 °C, when n.m.r. analysis suggested the reaction was complete. The mixture was poured into iced water (10 cm^3) which was extracted with dichloromethane. The organic phase was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to afford a yellow oil (2.54 g); $\delta_H(CCl_4)$ 1.65—2.40 (4 H, m), 3.12 (2 H, dd, *J* 14.5, 8.3 Hz), 3.31—3.43 (2 H, m), 3.91 (2 H, br s), and 7.18—7.55 (10 H, m). This is consistent with the assigned structure, but the crude product was not purified.

The crude sample from above (2.54 g, 6.9 mmol) was dissolved in dichloromethane (25 cm^3), stirred in an ice-bath, treated with 3-chloroperoxybenzoic acid (85%; 5.68 g, 28.0 mmol) over 0.5 h, stirred 1 h at room temperature, and treated with saturated aqueous sodium metabisulphite (10 cm^3) and sodium hydrogen carbonate (10 cm^3). The phases were separated, the aqueous was extracted with dichloromethane, and the combined organic phases were dried ($MgSO_4$), and concentrated under reduced pressure to afford 2,5-dichloro-1,6-bisphenylsulphonylhexane as a pale yellow oil (2.19 g).

The crude material from above (2.10 g, 4.82 mmol) was dissolved in dimethyl sulphoxide (10 cm^3) containing anhydrous sodium acetate (1.58 g, 19.3 mmol), stirred for 2 h at room temperature and poured into iced water (20 cm^3). The mixture was extracted with dichloromethane, and the combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure to afford the title compound as a pale yellow oil, which crystallised with time (2.00 g, 55% based on thiophenol), m.p. 123—123.5 °C (from EtOH) (Found: C, 59.6; H, 5.0; S, 17.5. $C_{18}H_{18}O_4S_2$ requires C, 59.65; H, 5.00; S, 17.69%); $\delta_H(CDCl_3)$ 2.40 (4 H, m), 6.34 (2 H, d, *J* 14.6 Hz), 6.91 (2 H, m), and 7.49—7.90 (10 H, m); *m/z* (c.i., CH_4), 363 (MH^+, 100%), 221 (28), 143 (19), 125 (14), and 111 (16).

Analysis of [1,6-$^2H_2$]*Hexa*-1,5-*diene from Photolysis.*—Generally, the concentrated solution of hydrocarbon products, obtained as in the 'general procedure' above was titrated with a slight excess of benzenesulphenyl chloride until the yellow colour persisted. The adduct was converted into the bis-sulphone (**5**) by the above procedure, any crystallisations being avoided which might fractionate regioisomers or diastereoisomers and thus fractionate deuterium. The final product was recrystallised from ethanol to constant m.p. and then analysed by m.s. Recrystallisation and m.s. analysis were repeated until consistent data were obtained.

Isolation and Pyrolysis of [2,3-$^2H_2$]*Bicyclo*[2.2.0]*hexane.*—[$^2H_2$]-DBO (252 mg, 2.25 mmol) in pentane (20 cm^3) was irradiated and worked up as in the 'general procedure' to the end of the alumina column. The pentane solution was cooled to −78 °C, and ozone was passed in until n.m.r. analysis of an aliquot showed the absence of olefinic resonances. The sample was allowed to warm to room temperature and resubmitted to the 'general procedure' starting with a second alumina column. G.c. and ^2H n.m.r. analysis of the concentrated solution showed no signals not attributable to bicyclohexane. A solution of [2,3-$^2H_2$]bicyclo[2.2.0]hexane prepared as above, and which showed a ratio of *exo* to *endo* deuterium of 77:23, was diluted to 20 cm^3 with pentane, sealed under nitrogen in a Carius tube, heated for 21 h at 180 °C (*ca.* 10 half lives of the cleavage reaction,[6]) and resubmitted to the 'general procedure'. ^2H N.m.r. analysis at this stage showed *E*:*Z* deuterium to be 50:50.

This sample was subjected to the sulphur chemistry described above, at which stage the final product was analysed in the usual way by m.s.

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